

Obtaining of niobium-containing ferroalloys from the Russian ore raw materials

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Abstract. The possibility of processing niobium-containing pyrochlore-apatite concentrates obtained from ores of Beloziminskoye deposit has been studied. A two-stage scheme for selective reduction of phosphorus into a metal phase to obtain low-phosphorus niobium-containing slag was suggested. The reduction of phosphorus and iron was carried out by a carbothermic method using coke and pig iron carbon as the reducing agent. Pig iron chip and magnetite product (80 % Fe₂O₃) were used as the precipitating agent. In laboratory and semi-industrial conditions the basic possibility of selective separation and sedimentation of phosphorus (to 91 %) and iron from a niobic concentrate without considerable reduction of niobium (up to 1–2 %), according to the two-stage scheme with minimum possible temperature of process during the first period (~ 1260 °C) and hot soak at the increased temperature (~ 1450 °C) during the second period were shown. Obtained low-phosphorus niobium-containing slag after crushing can be used for ferroniobium production according to existing technological schemes.

1. Introduction

Among the main problems of Russian ferroalloy production, the availability of ore raw materials is becoming increasingly important. This is due to deterioration of quality and decreasing of ore raw materials reserves with increase of demand for ferroalloys of high standards. Only a few types of alloys are produced at domestic plants from their own raw materials, and the major part of them is either imported from abroad or melted from imported raw materials [1–3].

One of the most strategically important elements of metallurgical production is niobium [4–6]. Consumption of ferroniobium by Russian steelmakers increased from 200–300 tons/year in the late 1990s to 4–6.5 thousand tons/year at present. However, its own production in the Russian Federation is only ~ 200 tons/year due to the absence of modern technological solutions for processing raw materials from available domestic niobium deposits [7,8].

In the Russian Federation a large area of niobium deposits (Beloziminsky, Veletagninsky, Shtikhinsky, etc.) has been explored, in the Chitinsky region – Katuginsky, in the Krasnoyarsk region – Tatar, Chuktugon, etc. All deposits differ from each other in their physical composition, which includes pyrochlore, apatite, monacite, vermiculite and other minerals [8].

According to [8], promising industrial sources of this raw material can be divided into three groups:

1. The Objects of the accelerated development. These include the Tatar deposit (Krasnoyarsk Krai) represented by industrial minerals: pyrochlor, apatite and vermiculite; Sallanlatva (Murmansk Region), minerals: lueshite, barite.



2. Objects of complex industrial development with associated pyrochlore. This is Katugin deposit (Chitinsky Region), minerals: gagarinite, pyrochlore, colombian, zircon, cryolyte.

3. The super-large and large objects with leading pyrochlore specialization and naturally alloyed Fe-Nb ores. These include deposits: Tomtorskoe (Saha-Yakutia), pyrochlore, monacite, crandallite, etc.; Veletagninsky (Irkutsk Region), pyrochlore, apatite; Beloziminsky (Irkutsk Region), pyrochlore, apatite, Colombian, Monacite.

The content of Nb_2O_3 in the ores varies from 0.1 to 1%, and there are also different amounts of phosphorus, thorium and other elements.

When enriching ores of these deposits the concentrates of different composition are obtained, Nb_2O_3 content in which varies from 15–25 to 40–50%, phosphorus up to 10–15% [9].

In this regard there are difficult tasks to develop for each type of Russian ore raw material effective processes for obtaining niobium ferroalloys acceptable for steelmakers.

In the work [10,11] the technology of smelting ferroniobium and niobium-containing alloys from concentrates of ore of Veletagninskoye deposit is considered. For processing pure niobium pentoxide the out-of-furnace aluminothermal melting is proposed. One-stage electro-furnace aluminothermal smelting is proposed for processing of pre-dephosphorized concentrates. Two-stage scheme is proposed for processing concentrates with high content of phosphorus. At the first stage dephosphoration is carried out by conversion of phosphorus into associated metal and production of low-phosphorus niobium-containing slag. In the second step a niobium-containing alloy is produced from the low-phosphorus niobium-containing slag.

2. Experimental part

IMET UB RAS studied the possibility of processing pyrochlore-apatite concentrates obtained from the ores of the Beloziminsky deposit. The scheme of enrichment of these ores provides for production of rough and conditioned concentrates.

The task of the research was to develop physical and chemical bases and technology of the process of obtaining niobium ferroalloys of rational composition with deep dephosphoration.

On the basis of the studies carried out it was concluded that pyroselection using three main reduction methods (carbo-, alumino- and silicothemy) can be used to obtain complex niobium-containing alloys with deep Dephosphoration.

Dephosphoration of ore concentrates of Beloziminskoye deposit was carried out by pyroselection method.

The process was studied with a conditioned Belozimine concentrate (Table 1) [12].

Table 1. Composition of niobium concentrate, %.

Material	Nb_2O_5	P_2O_5	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	TiO_2
Conditioned concentrate	47.1	1.2	8.8	1.5	15.8	0.2	1.2	5.1

Composition of charge materials is given in Table 2.

Charge material size: conditioned concentrate – 0.3–1.2 mm, Coke – up to 3 mm, Ferrosilicon, silicoaluminium and aluminium– 0.5–2 mm, Pig iron chip – 0.2–0.4 mm, Lime, quartzite and hydrofluoric spar – 2–3 mm.

The difficulty of pyroselection is due to the fact that as a result of melting, it is necessary to leave niobium almost completely in the slag during deep reduction and transition of phosphorus in metal. At the same time selective reduction is a complex physical-chemical complex of processes of reducing various oxides, interaction of reduced metal globules with each other and with slag, coagulation of metal droplets, their deposition, etc.

Under laboratory conditions the physical and chemical characteristics of concentrates and the influence of various factors (amount and type of reducing agent, flux and precipitating agent, melt viscosity, process temperature, its duration) on the selective reduction of iron and phosphorus, ensuring the production of slag with $\text{Nb/P} > 20$, were studied.

The viscosity of the concentrate decreased sharply at 1350 °C, reaching $< 0.1 \text{ N}\cdot\text{s}/\text{m}^2$, the addition of fluorspar and alumina (the latter to a lesser extent) reduced the viscosity, the melting range decreased by 40–50°C.

Table 2. Chemical composition of charge materials, %.

Material name	C	A ^c	V ^r	W ^a	Si	Al	Fe	SiO ₂	CaO	CaF ₂	Al ₂ O ₃
Coke	84.6	7.6	2.7	5.1	–	–	–	–	–	–	–
Semi-coke	53.0	27.0	7.0	8.6	–	–	–	–	–	–	–
Aluminium	–	–	–	–	0.3	99.6	0.2	–	–	–	–
Pig iron chip	4.4	–	–	–	–	–	ost.	–	–	–	–
Lime	–	–	–	–	–	–	–	–	91.1	–	–
Quartzite	–	–	–	–	–	–	–	97.5	–	–	–
Fluorspar	–	–	–	–	–	–	–	–	–	92.0	–
Alumina	–	–	–	–	–	–	–	–	–	–	98.7

The feasibility of two-stage smelting was determined. Iron and phosphorus were reduced at 1260–1450 °C at the 1st stage. At the 2nd stage after completion of reduction reaction at the temperature of 1410–1450°C the melt viscosity was reduced and metal globules were precipitated.

As a precipitator, pig iron chip and magnetite product (80% Fe₂O₃) were tested in an amount of 2 to 15 and 3.6 to 26.8 g per 100 g concentrate, respectively (equal amount of Fe), and the amount of coke carbon and pig iron was taken based on the reduction of P and Fe (Figure 1 and 2).

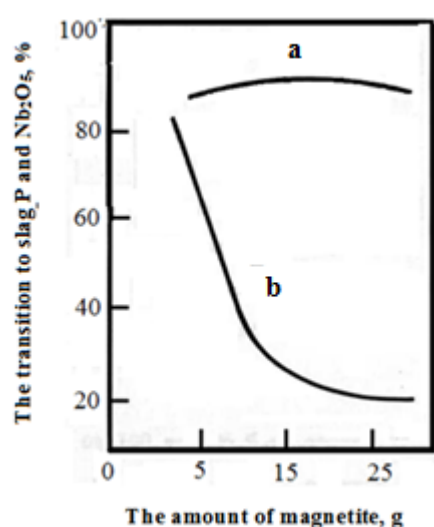


Figure 1. Transition of niobium (a) and phosphorus (b) to slag, depending on the amount of magnetite product.

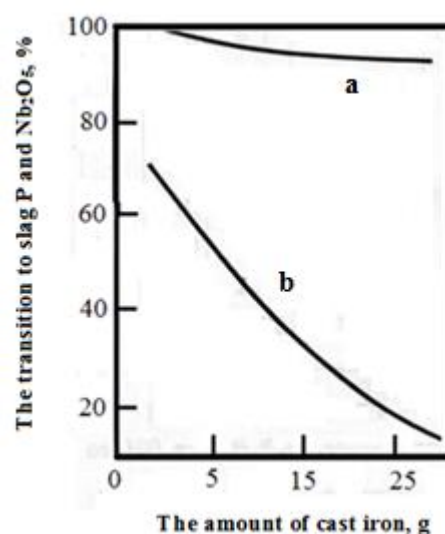


Figure 2. Transition of niobium (a) and phosphorus (b) to slag, depending on the amount cast iron in the charge.

In melts with magnetite product the dephosphoration of concentrate was quite complete, but niobium losses were also significant due to the increased amount of coke in the charge (on reduction of magnetite iron), reacting with oxides in the upper layers at the melt-coke boundary. In pig iron chip the phosphorus content decreased with increasing pig iron without significant transition of niobium to metal. The optimal amount of charge materials was determined experimentally: coke not less than stoichiometrically required for reduction of iron and phosphorus, pig iron chip ~ 15% of the concentrate weight.

It has been shown that it is possible by carbothermic reduction to selectively separate and precipitate phosphorus and iron from the conditioned niobium concentrate to the required limits with a slight reduction of niobium (up to 1–2%) according to a 2-step scheme: the mixture of concentrate,

coke and pig iron chip was being melted in an electric furnace at 1260–1300 °C for about 40 minutes, then the temperature was raised to 1410–1450 °C and was being held for 20–25 minutes. This scheme was recommended for further semi-industrial tests. The resulting dephosphorized slag after crushing can be used to melt [13, 14] ferroniobium or other niobium ferroalloys according to known technologies.

Semi-industrial experiments were carried out in a double-electrode electric furnace with a transformer capacity of 50 kVA lined with magnesite brick. 12 heats were performed.

Smelting showed that selective reduction of P and Fe (up to 91% P is removed into the metal) can be carried out in the electric arc furnace without significant reduction of niobium. Optimal for pyroselection was a step process with a minimum temperature in the first period (~ 1260 °C) and an increased (~ 1450 °C) in the second. Phosphorus removal was carried out to low values (~ 0.15% P in slag). An important condition for successful pyroselection in the electric arc furnace was the selection of electric parameters of smelting, as it depended on the degree of local overheats, the catch of elements, carbon participation in reduction. The best pyroselection results are obtained with an excess of carbon in the charge of 30% (from stoichiometrically required for reduction of P and Fe).

Industrial smelting on dephosphorization by pyroselection of conditioned concentrates was carried out in a furnace with a transformer capacity of 1100 kVA.

The raw material was a conditioned niobium concentrate ($\text{Nb}_2\text{O}_5 = 38.0\%$; $\text{P}_2\text{O}_5 = 4.5\text{--}6.4\%$; $\text{Fe}_2\text{O}_3 = 11.4\text{--}14.6\%$), pig iron chip and coke (68–73% C).

To achieve in slag a low phosphorus content (< 0.5%) upon condition of insignificant reduction of niobium it was necessary to have excess of reducer of 20–40% in furnace charge.

3. Conclusions

Satisfactory results were obtained. The electricity consumption per 1 ton of slag ranged from 1600–1900 to 970–1060 kWh. The content of phosphorus in the slag was quite low: 0.1–0.3% at $\text{Nb}_2\text{O}_5 = 34\text{--}39\%$, about 99% of phosphorus passed into the metal and into the gas phase, reduction and transition of niobium to metal was less than 1%. A total of 3 tonnes of slag was produced.

Industrial technology showed the fundamental possibility of dephosphorisation by pyroselection in an electric furnace with satisfactory characteristics.

Obtained low-phosphorus niobium-containing slag can be used for ferroniobium production after crushing, according to existing technological schemes.

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